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(54) Title: POROUS SILICA THIN FILM

(72) Inventor: Hiroyuki Hanabata  
Asashi Chemical Industry Co., Ltd.  
2-1 Samashima, Fuji-shi, Shizuoka-ken

(72) Inventor: Takaaki Ioka  
Asashi Chemical Industry Co., Ltd.  
2-1 Samashima, Fuji-shi, Shizuoka-ken

(71) Applicant: Asashi Chemical Industry Co., Ltd.  
1-2-6 Dojimahama, Kita-ku, Osaka-shi, Osaka-fu

(74) Agent: Hideo Takei, patent attorney, and 3 others

[There are no amendments to this patent application.]

(57) Abstract

### Objective

To provide a type of porous silica thin film with low moisture absorbability and excellent mechanical strength.

### Means to solve

The present invention provides a type of porous silica thin film with the following features: the porosity of the porous silica is high; the pores are of nanometer size; there is a prescribed amount of Si-CH<sub>3</sub> bonds in the structure; and the mobility of the CH<sub>3</sub> group is suppressed appropriately.

### Claims

1. A porous silica thin film characterized by the following facts: it is a porous silica thin film having pores in the silica structure; the porosity is in the range of 30-80%; the maximum pore size is 10 nm or smaller; the film contains 2 wt% or more of CH<sub>3</sub> groups bonded with Si atoms with a relaxation time in the structure in the range of 0.5-10 sec; and the film thickness is in the range of 0.1-10  $\mu$ m.
2. The porous silica thin film described in Claim 1, characterized by the fact that the porosity of the porous silica thin film is in the range of 40-70%.
3. The porous silica thin film described in Claim 1 or 2, characterized by the fact that the relaxation time of the carbon in the CH<sub>3</sub> group is in the range of 0.7-3 sec.
4. The porous silica thin film described in any of Claims 1-3, characterized by the fact that the film thickness is in the range of 0.5-5  $\mu$ m.
5. A multi-layer wiring structure, characterized by the fact that the structure includes multiple insulating layers and the wiring formed on them, with at least one of the insulating layers being made of the porous silica thin film described in any of Claims 1-4.
6. A semiconductor element including the multi-layer wiring structure described in Claim 5.

### Detailed explanation of the invention

[0001]

#### Industrial application field

The present invention pertains to a porous silica thin film used for insulating film. More specifically, the present invention pertains to a porous silica thin film for insulating film with a

large film thickness, low dielectric constant, excellent adhesivity and mechanical strength, and low moisture absorbability.

[0002]

Prior art

Since porous silica is light and has excellent heat resistance and other characteristics, it is widely used for structural materials, catalyst carriers, optical materials, etc. For example, in recent years, there has been great expectations on porous silica because it can lower the dielectric constant. The conventional compact silica film has been used as the raw material of insulating film for multi-layer wiring structures of LSI or other semiconductor elements. In recent years, the wiring density of LSI has been further increased, and thus the distance between adjacent wirings on the substrate is reduced. In this case, if the dielectric constant of the insulator is high, the electrostatic capacitance between the wirings will be increased. As a result, the electrical signals sent through these wirings will be significantly delayed. In order to solve this problem, there is a high demand on using a substance with a low dielectric constant as the raw material of the insulating film used for the multi-layer wiring structure. Since porous silica is a complex formed with air with a dielectric constant of 1, its dielectric constant can be significantly lowered compared with pure silica, which has a dielectric constant of 4.0-4.5. Also, since porous silica has the same degree of processibility and heat resistance, it has attracted a lot of attention as an ideal material for insulating film.

[0003]

Typical examples of porous silica include silica xerogel and silica aerogel. These raw materials are manufactured by the sol-gel reaction. The sol-gel reaction is the process of converting into a solid gel by using a colloidal substance, which is prepared by dispersing the particles known as a sol in a liquid, as an intermediate. In the case of silica, for example, when an alkoxysilane compound is used as raw material, the particles of the crosslinked structure obtained from hydrolysis and condensation of this raw material are dispersed in water to obtain a sol. A solid network containing a solvent is then formed as a gel from the hydrolysis and condensation of the particles. When the solvent is removed from the gel, leaving the solid network by itself, a silica xerogel structure is obtained.

[0004]

Japanese Kokai Patent Application No. Hei 7[1995]-257918 disclosed an example of forming a silica xerogel thin film. After a coating solution of a silica precursor, which is a sol, is prepared, it is coated on a substrate by means of spray coating, dip coating, or spin coating to

form a thin film with a thickness of several  $\mu\text{m}$  or thinner. After the thin film is gelled to obtain silica, it is dried to obtain the silica xerogel. Silica aerogel is different from silica xerogel in that the solvent in the silica is removed in the supercritical state. However, they are the same with respect to preparing the coating solution of the silica precursor, which is a sol.

[0005]

US Patent No. 5,807,607 and US Patent No. 5,900,879 also disclosed examples of forming silica xerosilica thin films. In this case, a special solvent, such as glycerol, is added into the solution when preparing the coating solution of the silica precursor, which is a sol. In this way, the pore size and the pore size distribution of the silica xerogel obtained by gelling and removing the solvent can be controlled, and the mechanical strength of the porous material can be increased. In this case, however, since a solvent with a low boiling point is used, the solvent is quickly removed when the pores are formed. Therefore, the wall parts that surround the holes cannot follow the capillary force generated. As a result, the pores shrink. Consequently, the pores either collapse, or microcracks appear around the pores. When an external stress is applied, the stress is concentrated on these cracks. Therefore, the mechanical strength of the silica xerogel is not sufficient. Although it is possible to significantly delay the speed of removing the solvent, it will take a long time to manufacture the silica xerogel.

[0006]

In order to solve the problem of the aforementioned solvent with a low boiling point, using an organic polymer instead of the solvent with a low boiling point has been attempted. When using an organic solvent, there is no need to strictly control the solvent's volatilizing speed or the atmosphere. For example, as described in Japanese Kokai Patent Application No. Hei 4[1992]-285081, the processing of the alkoxysilane sol-gel component is carried out in the presence of a specific organic polymer to manufacture a silica/organic polymer complex. The organic polymer is then removed to obtain a porous silica with a uniform pore size. Japanese Kokai Patent Application No. Hei 5[1993]-85762 and Publication Pamphlet No. WO99/03926 also disclosed a method of manufacturing a porous silica with very low dielectric constant as well as with uniform pores and pore distribution from the mixture of an alkoxysilane and organic polymer. In addition, according to Japanese Kokai Patent Application No. Hei 10[1998]-25359 and Japanese Kokoku Patent No. Hei 7[1995]-88239, the fine particles of an organic polymer are dispersed in an oligomer of a metal alkoxide containing an alkoxysilane to generate a gel. The fine particles of the organic polymer are then removed by sintering to obtain a porous silica with a controlled pore system.

[0007]

As a means for solving the problem of the aforementioned solvent with a low boiling point, an organic polymer is used instead of the solvent with a low boiling point to delay removal of the fluid present around the pores as much as possible, to reduce the capillary force. When using an organic polymer, there is no need to strictly control the solvent's volatilizing speed or the atmosphere. For example, as described in Japanese Kokai Patent Application No. Hei 4[1992]-285081, the processing of the alkoxysilane sol-gel component is carried out in the presence of a specific organic polymer to manufacture a silica/organic polymer complex. The organic polymer is then removed to obtain a porous silica with a uniform pore size. Japanese Kokai Patent Application No. Hei 5[1993]-85762 and Publication Pamphlet No. WO99/03926 also disclosed a method of manufacturing a porous silica with a very low dielectric constant as well as with uniform pores and pore distribution from a mixture of alkoxysilane and organic polymer. Also, as described in Japanese Kokai Patent Application No. Hei 9[1997]-315812, a coating solution comprised of fine silica particles and a specific alkoxysilane and its hydrate is used to improve the adhesivity, mechanical strength, and other characteristics of the insulating film. In addition, according to Japanese Kokai Patent Application No. Hei 10[1998]-25359 and Japanese Kokoku Patent No. Hei 7[1995]-88239, the fine particles of an organic polymer are dispersed in an oligomer of a metal alkoxide containing an alkoxysilane to generate a gel. The fine particles of the organic polymer are then removed by sintering to obtain a porous silica with a controlled pore system.

[0008]

These methods, however, cannot provide adhesivity and mechanical strength that meet the requirements in practical applications. As described in Japanese Kokai Patent Application No. Hei 9[1997]-169845, an organic trialkoxysilane is used as the raw material, and the water amount as well as the reaction temperature in the sol-forming reaction can be controlled in order to improve the hardness and adhesivity of the bulk-form silica film. In this manufacturing method, however, only high-density silica, that is, silica with a high dielectric constant, is obtained. Also, since there is no control over the pore size and the pore size distribution at all, it is very difficult to improve the adhesivity and mechanical strength of the porous material. Japanese Kokoku Patent No. Hei 8[1996]-29952 disclosed a method of adding an organic polymer into a homogenous system. However, since phase separation occurs in the system at the time of gelling, it is unable to form pores with a submicron size in this case. In addition, it is also difficult to obtain a high mechanical strength.

[0009]

Another method for improving the mechanical strength of the porous material is to add a metal oxide other than silica. As described in Japanese Kokai Patent Application No. Hei 7[1995]-185306, an alkoxysilane, metal alkoxide, and halide other than silica are hydrolyzed to obtain an argogel. Then, the obtained argogel is dried in the supercritical state to obtain an aerogel. This patent used the aforementioned manufacturing method to improve the moisture resistance and mechanical strength. However, when using a metal alkoxide and halide other than silica, since these raw materials and/or their hydrates or condensation products lack the proper solubility in the sol-gel reaction, the system may become a slurry consisting of large-sized particles, or a precipitate is generated. In either case, only heterogeneous silica can be obtained. As a result, the generated material is inappropriate for an insulating film for the same reason explained above when fine particles of an organic polymer are added. As described above, it has been impossible to produce an insulating film for a multi-layer wiring structure used as a semiconductor element with a low dielectric constant, high adhesivity and mechanical strength, and low moisture absorbability. Also, none of the aforementioned references mentioned the concept that increasing the thickness of the thin film is considered very important as a practical characteristic, nor did they describe any specific method.

[0010]

Problems to be solved by the invention

The objective of the present invention is to solve the aforementioned problems by providing a porous silica thin film for insulating film with a large film thickness, low dielectric constant, excellent adhesivity and mechanical strength, and low moisture absorbability.

[0011]

Means for solving the problems

In order to realize the aforementioned objective, the present inventors have performed extensive research. As a result of this research work, it was found that a porous insulating film with a low dielectric constant, low moisture absorbability, and high adhesivity and mechanical strength can be obtained by including a prescribed amount of Si-CH<sub>3</sub> bonds in the structure of a porous silica thin film and by appropriately suppressing the mobility of the CH<sub>3</sub> groups in the porous silica thin film, which has a high porosity and pore size on the nanometer level. It was also found that the film thickness can be increased by adjusting the composition of the coating solution used for forming the thin film. The present invention was achieved based on the conventional research. Consequently, the purpose of the present invention is to provide an insulating film material with a low dielectric constant, excellent adhesivity and mechanical

strength, low moisture absorbability, and practical film thickness, and to provide the applications of such material.

[0012]

The aforementioned objective and other objectives as well as various characteristics and benefits of the present invention will be clarified from the detailed explanation to be provided below. In order to make the present invention easy to understand, the basic characteristics of the present invention and the preferable embodiments of the present invention will be described.

1. A porous silica thin film characterized by the following facts: it is a porous silica thin film having pores in the silica structure; the porosity is in the range of 30-80%; the maximum pore size is 10 nm or smaller; the film contains 2 wt% or more of CH<sub>3</sub> groups bonded with Si atoms with a relaxation time in the structure in the range of 0.5-10 sec; and the film thickness is in the range of 0.1-10 μm.

2. The porous silica thin film described in 1, characterized by the fact that the porosity of the porous silica thin film is in the range of 40-70%.

3. The porous silica thin film described in 1 or 2, characterized by the fact that the relaxation time of the carbon in the CH<sub>3</sub> group is in the range of 0.7-3 sec.

4. The porous silica thin film described in any of 1-3, characterized by the fact that the film thickness is in the range of 0.5-5 μm.

5. A multi-layer wiring structure characterized by the fact that the structure includes multiple insulating layers and the wiring formed on them, with at least one of the insulating layers being made of the porous silica thin film described in any of 1-4.

6. A semiconductor element including the multi-layer wiring structure described in 5.

[0013]

In the following, the present invention will be explained in detail. The silica used in the specification of the present invention includes those represented by the following structural formula having hydrocarbon or hydrogen atoms on [bonded to] silicon in addition to silicon oxide (SiO<sub>2</sub>).



(where R<sup>1</sup> represents a C1-8 straight, branched, or cyclic alkyl group or aromatic group, 0 ≤ x ≤ 2, and y is 0 or 1).

The porous silica thin film of the present invention is characterized by having a porosity of 30-80%. The effect of the present invention can be better displayed if the porosity is in the range of 40-70%. Although the porosity is also dependent on the chemical structure of silica, if it is lower than 30%, the dielectric constant becomes too high, thus it is inappropriate to use the porous

silica thin film as an insulating film. On the other hand, if the porosity is higher than 80%, the adhesivity and the mechanical strength cannot reach practical levels.

[0014]

In order to improve the mechanical strength and the adhesivity of the porous silica thin film, it is important to control the pore size and the pore size distribution of the porous material. Generally speaking, when a porous material has large pores, there are defective points where stress is concentrated. As a result, a high mechanical strength cannot be obtained. In some cases, the structure itself will be destroyed due to the occurrence of microcracks. Although it is believed that the large pores are caused for various reasons, according to reference "Sol-Gel Science (by C. J. Brinker & G. W. Scherer, Academic Press, published in 1990)", when the granular silica sol as the constituent unit of silica has a large particle size, large pores can be easily formed between the particles. The porous silica thin film disclosed in the present invention only has small pores with a maximum pore size of 10 nm or smaller. The reason is believed to be that the sol particles can be filled most compactly because the sol particle size is small and uniform. Also, since there is no place where stress is concentrated, the high mechanical strength is not deteriorated.

[0015]

In addition to increasing the mechanical strength, strengthening the structure of the porous gel skeleton is as important as controlling the pore size. As to be described later, in order to improve the moisture absorbability, Si-CH<sub>3</sub> bonds are introduced into the structure of the porous silica thin film of the present invention. The relaxation time of carbon of the methyl group derived from <sup>13</sup>C-NMR is in the range of 0.5-10 sec, preferably in the range of 0.7-3 sec. When the relaxation time of the CH<sub>3</sub> group is in the aforementioned range, the mobility of the porous silica of the present invention is appropriately suppressed. In other words, the silica skeleton becomes compact. As a result, a high mechanical strength is displayed. If the relaxation time is shorter than 0.5 sec, the skeleton strength with respect to external stress is not high enough, and the mechanical strength becomes low. On the other hand, if the relaxation time is longer than 10 sec, the porosity of the porous silica thin film becomes lower than 30%, which is the lower limit of the present invention. As another characteristic of the present invention, the amount of the CH<sub>3</sub> groups coming from the Si-CH<sub>3</sub> bonds in the silica gel thin film is at least 2 wt%. In this way, the moisture absorbability can be significantly improved. If the methyl group content is less than 2 wt%, the moisture absorbability will be significantly deteriorated.

[0016]



In the following, the method for manufacturing the porous silica thin film of the present invention will be explained. Examples of the alkoxysilane that can be used in the present invention include methyltrimethoxysilane, methyltributoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane or methylethyldimethoxysilane, methylethyldiethoxysilane, etc., among which trimethylmethoxysilane and trimethylethoxysilane are preferred. The content of the alkoxysilane in the porous silica thin film as the final product must be at least 2 wt% measured in [terms of] the weight of Si-CH<sub>3</sub> groups. If the content is less than 2 wt%, the moisture absorbability will be significantly deteriorated. When the amount of CH<sub>3</sub> groups is more than 22 wt%, the mechanical strength can deteriorate.

[0017]

Examples of an alkoxysilane having groups other than a methyl group that can be used in the present invention include tetramethoxysilane, tetraethoxysilane, tetra(n-propoxy)silane, tetra(i-propoxy)silane, tetra(n-butoxy)silane, tetra(t-butoxy)silane, trimethoxysilane, triethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, bis(trimethoxysilyl)methane, bis(triethoxysilyl)methane, 1,2-bis(trimethoxysilyl)ethane, 1,4-bis(trimethoxysilyl)benzene, 1,4-bis(triethoxysilyl)benzene, etc., among which tetramethoxysilane, tetraethoxysilane, trimethoxysilane, and triethoxysilane are preferred. It is also possible to use partial hydrates of alkoxysilanes as the raw material.

[0018]

In order to modify the obtained porous silica thin film, it is also possible to mix an alkoxysilane having 2-3 hydrogen atoms, alkyl groups, or aryl groups on [bonded to the] silicon atom with the aforementioned alkoxysilane. Examples include triethylmethoxysilane, triethylethoxysilane, tripropylmethoxysilane, triphenylmethoxysilane, triphenylethoxysilane, phenyldimethylmethoxysilane, phenyldimethylethoxysilane, diphenylmethylmethoxysilane, diphenylmethylethoxysilane, etc. The amount of this alkoxysilane used is 80 mol% or less with respect to the total molar amount of the alkoxysilane used as the raw material. If the amount is more than 80 mol%, the material may not be gelled in some cases.

[0019]

An organic polymer having at least one polymerizable functional group in its molecule can be used as the organic polymer in the present invention. There is no special limitation on the organic polymer as long as it has at least one polymerizable functional group in its molecular chain. Examples include a polyether, polyester, polycarbonate, polyanhydride, polyamide, polyurethane, polyurea, polyacrylic acid, polyacrylate, polymethacrylic acid, polymethacrylate,

polyacrylamide, polymethacrylamide, polyacrylonitrile, polymethacrylonitrile, polyolefin, polydiene, polyvinyl ether, polyvinyl ester, polyvinyl alcohol, polyvinylidene halide, polypolystyrene, polysiloxane, polysulfide, polysulfone, polyimine, polyimide, cellulose, and polymers mainly composed of the derivatives of the polymers listed above. It is also possible to use the copolymers of the monomers used as the constituent units of the aforementioned polymers or the copolymers formed with any other monomers. The organic polymers can be used either alone as a mixture of several types.

[0020]

The preferable examples among the polymers listed above include those mainly composed of a polyether, polyester, polycarbonate, polyanhydride, polyamide, polyurethane, polyurea, polyacrylic acid, polyacrylate, polymethacrylic acid, polymethacrylate, polyacrylamide, polymethacrylamide, polyvinylamide, polyvinylamine, polyvinyl ester, polyvinylalcohol, polyimine, and polyimide. Also, when performing conversion to porous silica by means of heating sintering as to be described later, it is particularly preferred to use the organic polymers mainly composed of an aliphatic polyester, aliphatic polyether, aliphatic polycarbonate, or aliphatic polyanhydride with low pyrolysis temperature.

[0021]

Examples of polymerizable functional groups include a vinyl group, vinylidene group, vinylene group, glycidyl group, allyl group, acrylate group, methacrylate group, acrylamide group, methacrylamide group, carboxyl group, hydroxyl group, isocyanate group, amino group, imino group, halogen group, etc. These functional groups can be bonded in the main chain or to the end or a side chain of the polymer. They can also be directly bonded to the polymer chain or via spacers, such as an alkylene group or ether group. The same polymer molecule may have one or several types of functional groups. Among the aforementioned functional groups, a vinyl group, vinylidene group, vinylene group, glycidyl group, allyl group, acrylate group, methacrylate group, acrylamide group, and methacrylamide group are preferred.

[0022]

Specific examples of the basic skeleton of the organic polymer that can be used in the present invention are listed below. In the following, alkylene refers to methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, isopropylidene, 1,2-dimethylethylene, and 2,2-dimethyltrimethylene. Alkyl refers to a C1-8 alkyl group and phenyl group, tolyl group, anyl group, or other aryl group. (Meth)acrylate refers to both acrylate and

methacrylate. Dicarboxylic acid refers to oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, or other organic acid.

[0023]

① Aliphatic polyethers having an acrylate group, methacrylate group, vinyl group, glycidyl group, or other polymerizable functional group at the terminals, such as polyalkylene glycol (meth)acrylate, polyalkylene glycol di(meth)acrylate, polyalkylene glycol alkyl ether (meth)acrylate, polyalkylene glycol vinyl ether, polyalkylene glycol divinyl ether, polyalkylene glycol alkyl ether vinyl ether, polyalkylene glycol glycidyl ether, polyalkylene glycol diglycidyl ether, polyalkylene glycol alkyl ether glycidyl ether, etc.

[0024]

② Polycaprolactones having an acrylate group, methacrylate group, vinyl group, glycidyl group or other polymerizable functional group at one or both terminals such as polycaprolactone (meth)acrylate, polycaprolactone vinyl ether, polycaprolactone glydicyl ether, polycaprolactone vinyl ester, polycaprolactone glycidyl ester, polycaprolactone vinyl ester (meth)acrylate, polycaprolactone vinyl ester vinyl ether, polycaprolactone glycidyl ester vinyl ether, polycaprolactone vinyl ester glycidyl ether, polycaprolactone glydicyl ester glycidyl ether, etc.

[0025]

③ (Meth)acrylate, di(meth)acrylate, tri(meth)acrylate, vinyl ether, divinyl ether, trivinyl ether, glycidyl ether, diglycidyl ether, triglycidyl ether of polycaprolactone triol.

④ Aliphatic polyesters, which are polymers of dicarboxylic acids and alkylene glycols and having an acrylate group, methacrylate group, vinyl group, glycidyl group, or other polymerizable functional group at one or both terminals.

⑤ Aliphatic polyalkylene carbonates having an acrylate group, methacrylate group, vinyl group, glycidyl group, or other polymerizable functional group at one or both terminals.

[0026]

⑥ Aliphatic polyanhydrides, which are polymers of dicarboxylic anhydrides and have an acrylate group, methacrylate group, vinyl group, glycidyl group, or other polymerizable functional group at the terminals.

⑦ Polyglycidyl (meth)acrylate, polyallyl (meth)acrylate, polyvinyl (meth)acrylate, and other polyacrylates or polymethacrylates having a vinyl group, glycidyl group, allyl group, or other functional groups in the side chain.

⑧ Polyvinyl cinnamate, polyvinyl azidobenzal, epoxy resin, etc.

Among those listed above, the aliphatic polyethers, aliphatic polyesters, aliphatic polycarbonates, and aliphatic polyanhydrides, etc., listed in said ①-⑥ are particularly preferred because they can facilitate the conversion to a porous silicon oxide performed by means of heating/sintering to be described later.

[0027]

The molecular weight of the organic polymer is preferably in the range of 100-1,000,000 on the average. It should be noticed that the size of the pores in the porous silica thin film is very small and uniform and has little dependency on the molecular weight of the organic polymer. The molecular weight of the organic polymer is very important for realizing high mechanical strength. The amount of the organic polymer used in the present invention is in the range of  $10^{-2}$  - 100 parts by weight, preferably, in the range of  $10^{-1}$  - 10 parts by weight, or more preferably, in the range of  $10^{-1}$  - 5 parts by weight. If the amount of the organic polymer added is less than  $10^{-2}$  parts by weight or more than 100 parts by weight, the characteristics of the porous material cannot be displayed, and the material lacks in practicability.

[0028]

In the present invention, water is needed in the hydrolysis of the alkoxysilane. The water can be added in the original liquid form or in the form of an alcohol or aqueous solution. It is also possible to add water in the form of vapor. If water is added too quickly, hydrolysis and condensation will be carried out at an excessively high speed, depending on the type of alkoxysilane, and thus a precipitate may be generated. Therefore, water should be added by taking sufficient time, or in the presence of an alcohol or other solvent for the purpose of homogenization, or at a low temperature. It is also possible to add a catalyst for accelerating the hydrolysis and the dehydrating condensation reaction of the alkoxysilane. Examples of the catalyst that can be used include hydrochloric acid, nitric acid, sulfuric acid, formic acid, acetic acid, oxalic acid, maleic acid, or other acid.

[0029]

The amount of the catalyst added is 1 mol or less, preferably  $10^{-1}$  mol or less, with respect to 1 mol of alkoxysilane. If the amount is more than 1 mol, a large amount of precipitate can be generated, and uniform porous material may not be obtained. In the present invention, the thin film is formed by coating the mixture prepared using the method described above on a substrate. The film forming methods include flow coating, dipping, spin coating, and other conventional methods. However, spin coating is preferred when manufacturing the insulating layer for the multi-layer wiring structure of the semiconductor element. The thickness of the thin

film can be controlled in the range of 0.1-10  $\mu\text{m}$ , depending on the viscosity of the composition and the rotation speed. If the film is thicker than 10  $\mu\text{m}$ , cracks may occur. The film thickness is usually in the range of 0.5-5  $\mu\text{m}$  when the film is used as an insulating layer for the multi-layer wiring structure of the semiconductor element.

[0030]

Although the presence of a solvent is not required when manufacturing the porous silica thin film of the present invention, if a solvent can dissolve both the alkoxysilane and the organic polymer, it can be used to such a degree that the characteristics of the thick porous material of the present invention are not adversely affected due to dilution of the entire solution by adding the solvent. Examples of the solvent that can be used include C1-4 monohydric alcohols, C1-4 dihydric alcohols, acetone, methyl ethyl ketone, and other ketones, glycerin, etc., and their ethers or esters, such as diethylene glycol, ethylene glycol monomethyl ether, ethylene glycol dimethyl ether, 2-ethoxyethanol, propylene glycol, monomethyl ether, propylene glycol methyl ether acetate or formamide, N-methylformamide, N-ethylformamide, N,N-dimethylformamide, N,N-diethyleformamide, N-methylacetamide, N-ethyleacetamide, N,N-dimethylacetamide, N,N-diethyleacetamide, N-methylpyrrolidone, N-formylmorpholine, N-acetylmorpholine, N-formylpyrrolidine, N-acetopyrrolidine, N,N'-diformylpiperazine, N,N'-diacetylpiperazine, and other amides,  $\gamma$ -butyrolactone and other lactones, tetramethylurea, N,N'-dimethylimidazolydinone, and other ureas. These solvents can be used either alone or as a mixture of several types. Among these solvents, it is preferred to use acetone, methyl ethyl ketone, C1-4 monohydric alcohols, etc., in consideration of increasing the film thickness because these solvents volatilize immediately after spin coating. In addition, as demanded, a photocatalyst-generating agent for providing photosensitivity, adhesion improving agent for improving the adhesion to the substrate, stabilizer for long-term storage, and other additives can be added into the composition of the present invention as long as the objective of the present invention is not adversely affected.

[0031]

A semiconductor substrate made of silicon, germanium, etc. or compound semiconductor substrate made of potassium-arsenic, indium-antimony, etc., can be used as the substrate. Thin films made of other materials can be formed on the surface of the substrate. In this case, in addition to aluminum, titanium, chromium, nickel, copper, silver, tantalum, tungsten, osmium, gold, platinum, and other metals, other materials that can be used to form the thin film include silicon dioxide, fluorinated glass, phosphorous glass, boron-phosphorous glass, borosilicate glass, polysilicon, alumina, titania, zirconia, silicon nitride, titanium nitride, tantalum nitride,

boron nitride, hydrogenated silsesquioxane, or other inorganic compounds, methyl silsesquioxane, amorphous carbon, fluorinated amorphous carbon, polyimides, and other organic polymers.

[0032]

The coating solution prepared as described above is formed into a thin film. When the silica sol in the thin film is gelled at 50-300°C, a silica/organic polymer complex (hybrid material) can be obtained. More preferably, the gelling temperature is in the range of 60-200°C. Gelling can be well carried out in that temperature range. If the temperature is lower than 50°C, since gelling cannot be well carried out, shrinkage occurs, and the mechanical strength of the structure is not high enough. In some cases, the organic polymer even bleeds out. If the temperature is higher than 300°C, undesired voids may occur in the hybrid material.

[0033]

The organic polymer plays an important role in forming the hybrid material of the present invention. Since the organic polymer is virtually left in the reaction system in the process of converting from a sol to a gel at a temperature in the range of 50-300°C, the gel can be formed while the sol particles keep the size and form in their original swelling state. When the organic polymer is removed from the hybrid material in a later step to form a porous material, a sufficient porosity can be obtained. Also, since the polymer has at least one polymerizable functional group in its molecule, the polymer in the sol is grafted or converted to IPN (three-dimensional network structure). As a result, an appropriate degree of intertwining occurs between the sol and gel. The intertwining compacts the structure of the hybrid material. Since that state is also maintained by the gel, after the organic polymer is removed, the silica skeleton is compacted.

[0034]

The porous silica thin film of the present invention is obtained when only the organic spacer is removed under heating at 300-500°C. While some organic polymers can be simply removed by means of evaporation, other organic polymers must be removed by means of sintering accompanied by the decomposition of the organic polymer. Although the removal temperature varies, it is preferably in the range of 300-450°C. If the temperature is lower than 300°C, the organic spacer cannot be removed well. Since an impurity of the organic compound remains, there is a danger of obtaining a porous silica thin film with a low dielectric constant. On the other hand, although a temperature higher than 500°C is preferred for improving the

strength, such a temperature is impossible in the LSI manufacturing process. The heating time is preferably in the range of 1 min to 24 h. If the time is shorter than 1 min, since the evaporation or decomposition of the organic polymer is not well carried out, the organic compound is left as an impurity in the obtained porous silica thin film, deteriorating the characteristics. Also, since pyrolysis or evaporation is usually completed within 24 h, it is meaningless to conduct sintering for longer than 24 h.

[0035]

The organic polymer can be removed in an inactive atmosphere, such as nitrogen, argon, or helium, or in the air or an acidic atmosphere containing oxygen gas. Usually, it is preferred to use an acidic atmosphere in order to reduce the removal time and temperature. If ammonia, hydrogen, etc., exist in the atmosphere, the silanol groups left in the silica will be hydrogenated or nitrified, lowering the moisture absorbability of the porous silica thin film and suppressing the increase in the dielectric constant.

[0036]

When the obtained porous silica thin film is treated by a silylating agent, the water absorbability can be suppressed, and the dielectric constant can be stabilized. Also, the adhesivity to other substances can be improved. Examples of the silylating agent that can be used include trimethylmethoxysilane, triethylethoxysilane, dimethyldimethoxysilane, dimethyldiethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, dimethylethoxysilane, methyldiethoxysilane, dimethylvinylmethoxysilane, dimethylvinylethoxysilane, diphenyldimethoxysilane, diphenyldiethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, and other alkoxysilanes, trimethylchlorosilane, dimethyldichlorosilane, methyltrichlorosilane, methyldichlorosilane, methylvinylchlorosilane, methylchlorodisilane, triphenylchlorosilane, methyldiphenylchlorosilane, diphenyldichlorosilane, and other chlorosilanes, hexamethyldisilazane, N,N'-bis(trimethylsilyl)urea, N-trimethylsilyl acetamide, dimethyltrimethylsilylamine, diethyltriethylsilylamine, trimethylsilyl imidazole, and other silazanes. The silylation can be carried out by means of coating, dipping, vapor exposure, etc.

[0037]

Since the structure of the porous silica thin film formed using the aforementioned method has a high porosity, small and uniform pore size, and strong silica skeleton, the adhesivity and mechanical strength are very high, and the moisture absorbability is low. Also, since the film thickness can be increased, the porous silica thin film is suitable for an insulating film formed on the substrate for LSI multi-layer wiring or for a semiconductor element. For example, a porous silica thin film with excellent practicability was obtained. The film thickness is 1.0  $\mu\text{m}$ . The porosity is 51%, and the dielectric constant is 2.0. The average pore size is 2.4 nm, and there is virtually no pore larger than 10 nm. The tensile strength is 40 MPa (adhesive force is 40 MPa or higher). After the film was set in an atmosphere with a relative humidity of 100% for 24 h, the dielectric constant was 2.05, which showed almost no change. The porous silica thin film provided by the present invention can also be used as bulky porous silica materials in addition to a thin film, such as an optical film or catalyst carrier, heat insulating material, absorbent, glass filling material, caking inhibitor, thickener, pigment, opaquer, ceramics, smoke inhibitor, grinding agent, dentifrice agent, etc.

[0038]

#### Embodiments of the invention

In the following, application examples of the present invention will be explained. The present invention, however, is not limited to these application examples. The porous silica thin film is evaluated using the following criteria.

(1) Porosity, average pore size, pore size distribution: The thin film on a silicon wafer was chipped and was measured using a nitrogen adsorption porosimeter (Auto Sov 1 produced by Kuantu Chrome Co., Ltd.). The porosity is derived by comparing with the density of a pre-prepared bulk. The pore size with the maximum pore size of  $10^{-3}$  or smaller measured as the  $V/r$  value was adopted.

(2) Dielectric constant: After a porous film was formed on a silicon wafer with TiN formed on its surface, aluminum was deposited through a mask made of SUS (stainless steel) on the thin film to form an electrode with a diameter of 1.7 mm. An impedance analyzer was used to measure the dielectric constant (k) at 1 MHz.

[0039]



(3) Content of CH<sub>3</sub>: A known amount of powder chipped from a silicon wafer was mixed with NaHCO<sub>3</sub> added in a certain weight ratio with respect to the powder. The mixture was subjected to a solid <sup>1</sup>H-NMR measurement, and the CH<sub>3</sub> content was derived from the signal areas of the aforementioned components. The <sup>1</sup>H-NMR measurement was conducted under the conditions of magic angle rotation (10000 Hz), pulse width 5 (μsec), delay time 10 (sec), number of times of integration: 100.

(4) Relaxation time of carbon in CH<sub>3</sub> group (T1ρC): T1ρC was derived by performing nuclear magnetic resonance analysis (MSL400, product of Bruker Co.) on the powder chipped from a silicon wafer. The measurement of T1ρC also used the methods of <sup>1</sup>H-<sup>13</sup>C cross polarization (CP), magic angle rotation (5000 Hz), and <sup>1</sup>H irradiation decoupling. The measurement was carried out at a delay time of 4 s and a contact time of 1 ms. With the spin lock varied, the measurement was conducted by 200 rounds of integration. T1ρC was derived from the obtained signal intensity.

[0040]

(5) Mechanical strength (adhesivity, tensile strength): Titanium was sputtered to a film thickness of 10 nm on a silicon wafer film. A rivet was adhered by epoxy resin on the titanium film, and 5 samples were prepared in this way. The adhesivity and tensile strength of the film were evaluated as the average value of the 5 samples measured by a tensile testing machine. The measurement temperature was 25°C.

(6) Moisture absorbability: The moisture absorbability was evaluated based on the difference in the dielectric constant before and after a sample was set in an atmosphere with a relative humidity of 100% for 24 h.

[0041]

#### Application Example 1

After 1.2 g (5.8 mmol) of tetraethoxysilane, 6.3 g (46.2 mmol) of methyltrimethoxysilane, and 5.2 g of polyethylene glycol monomethacrylate (molecular weight: 400) were dissolved in a solvent mixture consisting of 8.0 g of methanol, 3.0 g of γ-butyrolactone, and 2.0 g of propylene glycol methyl ether acetate, 2.5 g of water and 1.5 g of 0.1N sulfuric acid were added into the solution, followed by 2 h of stirring performed at room temperature. After 0.01 g of dicumyl peroxide was added into 3 g of the solution, the solution was coated by the spin coating method at a speed of 1300 rpm in 10 sec on a 6-inch silicon wafer, where a silicon nitride film had been preformed by means of the chemical vapor deposition method. After the wafer was heated at 1200°C in the air on a hot plate for 3 min, it was subjected to a heat

treatment carried out at 200°C in a nitrogen atmosphere for 1 h, then in a curing furnace at 450°C for 1 h. As a result, a 1- $\mu$ m-thick porous silica thin film was formed.

[0042]

The porosity of the obtained porous silica thin film measured by means of nitrogen adsorption was 51%, and the average pore size was 2.4 nm. There was virtually no pore larger than 10 nm. The dielectric constant at 1 MHz of a porous film formed in the same way on a TiN film was 2.0, which is much smaller than 4.5, the dielectric constant of SiO<sub>2</sub>. After the film was set in an atmosphere with a relative humidity of 100% for 24 h, the dielectric constant was 2.05. The concentration of CH<sub>3</sub> groups in the silica film was 19.7 wt%. The relaxation time of carbon in CH<sub>3</sub> was 1.5 sec. The silica skeleton was very strong. Also, the adhesivity and tensile strength of the obtained film was 40 MPa (since breakage was [indicates] cohesive damage of the material, it is believed that the adhesive force was 40 MPa or larger). This porous silica thin film has the desired film thickness, dielectric constant, fine pore size, fine pore distribution, high mechanical strength, and low moisture absorbability as a material for a semiconductor interlayer insulating film.

[0043]

#### Application Example 2

A coating solution was prepared in the same way as described in Application Example 1 except for using 4.8 g (23.0 mmol) of tetraethoxysilane and 4.2 g (30.8 mmol) of methyltrimethoxysilane, and a 1.1- $\mu$ m-thick porous silica thin film was formed. The dielectric constant of the porous film formed on a TiN film was 2.2. After the film was set in an atmosphere with a relative humidity of 100% for 24 h, the dielectric constant was 2.25. The average pore size of the thin film coated on a silicon wafer was 3.1 nm, and there was virtually no pore larger than 10 nm. The CH<sub>3</sub> content in the thin film was 11.5 wt%. The relaxation time of carbon in CH<sub>3</sub> was 2.5 sec. The silica skeleton was very strong. Also, the tensile strength was 45 MPa (the adhesive force was 45 MPa or larger). Consequently, the formed porous silica thin film has the desirable characteristics as a material for a semiconductor interlayer insulating film.

[0044]

A 0.95- $\mu$ m-thick silica thin film was formed in the same way as described in Application Example 1 except for using 5.2 g of polyethylene glycol dimethacrylate (molecular weight: 400) as the organic polymer. The dielectric constant of the porous film formed on a TiN film was 1.9. After the film was set in an atmosphere with a relative humidity of 100% for 24 h, the dielectric constant was 1.95. The average pore size of the thin film coated on a silicon wafer was 2.5 nm,

and there was virtually no pore larger than 10 nm. The CH<sub>3</sub> content in the thin film was 20.3 wt%. The relaxation time of carbon in CH<sub>3</sub> was 1.1 sec. The silica skeleton was strong enough to display a high mechanical strength. Also, the tensile strength was 41 MPa (the adhesive force was 41 MPa or larger). Consequently, the formed porous silica thin film has the desired film thickness, dielectric constant, fine pore size, fine pore distribution, and high mechanical strength as a material for a semiconductor interlayer insulating film.

[0045]

#### Comparative Example 1

A 1.1- $\mu$ m-thick silica thin film was formed in the same way as described in Application Example 1 except for using 12.0 g (57.6 mmol) of tetraethoxysilane and 10.4 g of polyethylene glycol monomethacrylate (molecular weight: 400). The dielectric constant of the obtained silica thin film was 2.0, and the tensile strength was 43 MPa (adhesive force was 43 MPa or larger). However, the dielectric constant increased to 3.5 after 24 h. Therefore, it is inappropriate to use this film as a material for an interlayer insulating film.

[0046]

#### Comparative Example 2

A 0.98- $\mu$ m-thick silica thin film was formed in the same way as described in Application Example 1 except for using 5.2 g of polypropylene glycol dimethyl ether (molecular weight: 500) as the organic polymer. The CH<sub>3</sub> content was 22.1 wt%, and the relaxation time was 0.41 sec. The adhesive force was 15 MPa (tensile strength was 15 MPa or larger). Therefore, it is inappropriate to use this film as a material for an interlayer insulating film.

[0047]

#### Comparative Example 3

After 12.0 g (58 mmol) of tetraethoxysilane, 6.8 g of polyethylene glycol monomethacrylate (average molecular weight: 360), and 3.4 g of polyethylene glycol dimethacrylate (average molecular weight: 540) were dissolved in a mixed solvent consisting of 20.0 g of N-methylpyrrolidone and 10.0 g of propylene glycol methyl ether acetate, 7.5 g of water and 1.5 g of 0.1N nitric acid were added into the solution, followed by 2 h of stirring performed at room temperature. Next, 0.5 g of dicumyl peroxide was added. The solution was rotation coated at a speed of 1500 rpm on a silicon wafer, followed by heating at 120°C for 1 h and at 180°C for 1 h. As a result, a composite thin film with a thickness of 0.41  $\mu$ m was formed. The sample was sintered at 450°C in a nitrogen atmosphere for 1 h to remove the organic polymer. As a result, a porous silica thin film was formed. In this way, only a very thin film

with a thickness of 0.23  $\mu\text{m}$  was formed. Also, after 24 h, the dielectric constant increased from 2.3 to 4.2.

[0048]

#### Effects of the invention

Since the structure of the porous silica thin film formed using the aforementioned method has a high porosity, small and uniform pore size, and strong silica skeleton, the adhesivity and mechanical strength are very high, and the moisture absorbability is low. Also, since the film thickness can be increased, the porous silica thin film is suitable for an insulating film formed on a substrate for LSI multi-layer wiring or for a semiconductor element.



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